Province of British Columbia
Ministry of Environment
ASSESSMENT AND PLANNING DIVISION

APD Bulletin 14

SHAWNIGAN LAKE WATERSHED STUDY: BACKGROUND REPORT 2

AN EVALUATION OF USE OF CERAMIC CUP SOIL WATER SAMPLERS IN NUTRIENT TRANSPORT STUDIES

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Victoria, B.C.
March, 1981

File No. ESD0273896

Canadian Cataloguing in Publication Data

Nagpal, N. K.
Shawnigan Lake watershed study : background report 2

(APD bulletin, ISSN 0228-5304 ; 14)

Bibliography: p.
ISBN 0-7719-8750-1

1. Lysimeter. 2. Soil pollution - British Columbia - Shawnigan Lake watershed. 3. Sewage disposal in the ground - British Columbia - Shawnigan Lake watershed. I. British Columbia. Ministry of Environment. Assessment and Planning Division. II. British Columbia. Aquatics Studies Branch. III. Title. IV. Series.

TD878.N33 628.5'5'0971134 C81-092372-6

SUMMARY

Ceramic cup lysimeters are commonly used for detecting nutrient movement in unsaturated soils. However, accuracy of results obtained from these lysimeters has been questioned. Guidelines for extraction of soil water samples have been proposed to minimize the effect of lysimeters on soil solution concentration.

The objective of this study was to evaluate use of commercially available porous cup lysimeters for soil solution extraction. Results indicated that ortho-P, (NO_3 + NO_2)-N, and potassium (K) are sorbed by the porous cup during extraction. As expected, the retention of (NO_3 + NO_2)-N was minimal. Also, screening of NO_3 by the cup was not obvious. Maximum retention of ortho-P and K was a function of solution concentration and the time of contact between solution and cup.

A rest period (24 hours) of no extraction appeared to enhance phosphorus sorption capacity of the ceramic cup. Furthermore, phosphorus sorption was reversible in nature. The porous cup subjected to high solution concentration initially released phosphorus when flushed with soil solution of low concentration.

The sorption of ortho-P and K decreased as the tension and number of samples extracted with the porous cup increased. In order to minimize the effect of porous cups, it is recommended that (a) soil water samples be extracted at high tensions, and (b) a number of water samples (two or more) be collected in succession, and samples collected later in the sequence be used to assess ionic concentration of soil solution.

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1. INTRODUCTION

Ceramic porous cup lysimeters or soil water samplers are a preferred means of sampling water from unsaturated soils. This is due in part to their commercial availability.

In studies related to migration of environmental contaminants through soil-water systems, the accuracy of results obtained from water samples extracted with ceramic porous cups has been questioned. Grover and Lamborn (1970) found that ceramic cups contribute excessive amounts of calcium, sodium, and potassium to water samples drawn through them. At the same time it was observed that the cups absorbed a significant amount of phosphorus from solutions containing phosphorus. Furthermore pre-leaching of the cups with 1N HCl reduced both phosphorus absorption and contamination of the water samples by sodium and potassium. Sorption and screening of phosphorus and nitrate ions by ceramic cups was also studied by Hansen and Harris (1975). They reported that the ionic concentration of the extracted water sample was a function of water intake rate of the porous cup, sample size, vacuum level, and initial solution concentration. Severson and Grigal (1976) indicated dependence of ionic concentration of the extracted water samples on length of extraction time. It was shown that as the extraction time increased, the extracted sample represented more closely the solution held by soil at tensions approaching those applied to the porous cup. In more recent work, Levin and Jackson (1977) reported observations that contradicted those of the earlier workers. While comparing results obtained with porous ceramic cups and Amicon hollow fibres, Levin and Jackson found that neither extractor altered the concentration of calcium, magnesium or orthophosphate-phosphorus during sample collection. Possible screening of nitrate-nitrogen by hollow fibres as well as ceramic cups was, however, indicated by their data. The latter observation corresponds with the results of Hansen and Harris (1975).

Several guidelines have been proposed to reduce variability in soil water samples collected with the porous ceramic cups. Severson and Grigal (1976) recommended that the lowest effective tension be applied to the cups during water sampling. A value of 0.1 bar was suggested as the upper limit of tension to be applied to monitor solutions that have potential for being lost from the soil system. Hansen and Harris (1975) suggested use of (a) ceramic cup lysimeters with similar intake rates where several samplers are used and results compared (b) short sampling intervals (c) uniform sampler lengths, and (d) the same initial vacuum for all samplers.

Based on the above indicated literature reports and recommendations, the soil water samplers used in a watershed study at Shawnigan Lake, B.C. were tested for their physical characteristics. During these tests, effects of initial solution concentration and tension level were investigated. Additional information as to the effects of fluctuating solution concentration and long-term contact between porous cup and ionic solution, on water samples was also sought, since this was of significance to normal soil water quality monitoring in septic tank drainfields.

2. MATERIALS AND METHODS

The soil water sampler units were made of PVC access tubing, 48 mm outside diameter and 1 mm wall thickness, with a round-bottomed porous ceramic cup cemented to one end. The other end of the tube was fitted with a two-hole neoprene plug. Two pieces of acrylic tubing were inserted in the plug; one to evacuate or pressurize the inside of the access tube and the other (which extended into the porous cup) to draw water collected in the access tube. The porous ceramic cups, 60 mm long and 48 mm in outside diameter, had a bubbling pressure in excess of 1.0 bar.

Three sets of experiments were carried out. In Experiment I a sampler unit was placed in a plastic container with 500 millilitres of solution of a known concentration. A tension of 0.1 bar was applied. This tension was maintained until 250 millilitres of water sample was collected inside the cup and access tube. Both the solution remaining outside the sampling unit and the solution collected inside the sampler were analysed for their chemical constituents. The process was repeated four times (referred to as four applications in the text); each time 500 millilitres of fresh solution was used. The experiment was carried out with four different solution concentrations and four soil water sampling units identified as #1, 2, 3 and 4. The porous cups were thoroughly washed with 1N HCl and rinsed with distilled water before the beginning of the experiment.

The second set of experiments (Experiment II) was similar in nature to that of Experiment I. However, a tension of 0.6 bar was used in these tests, instead of 0.1 bar as in the case of Experiment I.

In Experiment III, a porous cup was subjected to a sequence of loading (high solution concentration) and flushing (low solution concentration) events. A constant tension of 0.6 bars was applied. A maximum of two consecutive loadings or flushings was applied in a day. The porous cup was left dipped in the solution between all loading or flushing events. The experiment was carried out over a period of six days. At the end of each loading and flushing event, chemical analysis was performed on the original solution as well as the extracted solution.

The solutions for the above experiments were prepared by dissolving varying quantities of superphosphate (0-18-0), muriate of potash (60% potassium), and potassium nitrate in distilled water. The original and the extracted solutions were analysed for

orthophosphate-phosphorus (ortho-P), (nitrate + nitrite)-nitrogen ($(NO_3 + NO_2)$ -N), and potassium (K) by ascorbic acid reduction, cadmium reduction plus diazotization and flame photometric methods respectively (McQuaker, 1976).

3. RESULTS AND DISCUSSION

3.1 Experiment I and II

Tables 1 and 2 show percent retention of ortho-P, $(NO_3 + NO_2)$-N, and potassium (K) by the porous cups in Experiment I and II respectively. The negative values for retention (Tables 1 and 2) indicate a net release of the elements by the porous cups during the application.

In general, the data indicate maximum retention of ortho-P, $(NO_3 + NO_2)$-N and K by the porous cups during the first application, followed by a decrease in retention in subsequent applications. An exception to the generality was displayed by the results of sampler #4 in Experiment II (Table 2), which indicated zero retention for $(NO_3 + NO_2)$-N during all applications. The results also suggest possible release of $(NO_3 + NO_2)$-N and potassium from porous cups of soil water sampling units #1 and #2 during the third and fourth applications of Experiment I. These general trends appear to point out maximum equilibrium retention values for the samplers, specific to nutrient elements. Further evidence presented below indicate partial reversibility.

The retention of ortho-P by the porous cups appears to depend upon initial solution concentration and tension applied (Tables 1 and 2). In general the porous cups continue to absorb relatively high proportions of ortho-P in each application when subjected to low solution concentrations and low tensions. For instance, sampler #1 retained a much smaller proportion (6.2%) of ortho-P at the end of the fourth application when subjected to an initial solution concentration of 0.253 mg/l as compared to that retained by sampler #3 (22.2%) with an initial ortho-P concentration of 0.057 mg/l (Table 1). The relation of these differences to initial solution concentrations undoubtedly are affected by the sample extraction times which varied between samples at the same tension. A comparison of results for the samplers #3 and #4 (Table 1, Experiment I), for instance, showed higher ortho-P retention for #4 (66.0%) during the fourth application than #3 (22.2%), although initial ortho-P concentrations were of similar magnitude in both cases (0.057 and 0.053 mg/l for samplers #3 and #4 respectively). It should be noted that the sample extraction time or contact time was much longer for sample #4 (435 minutes) than for sample #3 (360 minutes). Similar conclusions can be drawn from the results obtained for Experiment II (Table 2).

TABLE 1

EXPERIMENT I: Retention of (nitrate + nitrite)-nitrogen, orthophosphate-phosphorus and potassium by ceramic porous cups in each of four applications for various solution concentrations. The soil water samplers were subjected to a tension of 0.1 bar.

Element	Solution Concentration (mg/l)	Percent Retention In Each Application			
		A_1	A_2	A_3	A_4
		Soil Water Sampler #1; CT = 370 min.			
$(NO_3 + NO_2)$-N	7.6	8.3	8.2	-1.8*	-1.8*
Ortho-P	0.253	89.8	17.3	3.2	6.2
K	41.5	8.3	8.3	-1.2*	0.0
		Soil Water Sampler #2; CT** = 450 min.			
$(NO_3 + NO_2)$-N	4.7	9.3	0.0	2.0	0.0
Ortho-P	0.163	97.4	96.9	55.5	25.9
K	27.4	15.3	4.4	2.9	0.7
		Soil Water Sampler #3; CT = 360 min.			
$(NO_3 + NO_2)$-N	2.0	6.2	0.0	-0.5*	0.5
Ortho-P	0.057	≈100.0	89.1	36.8	22.2
K	22.7	10.3	3.5	1.7	0.9
		Soil Water Sample #4; CT = 435 min.			
$(NO_3 + NO_2)$-N	0.81	6.8	1.2	1.3	0.0
Ortho-P	0.053	93.9	92.2	91.1	66.0
K	6.9	30.3	13.1	7.3	1.5

* Negative retention values indicate net release of element during application.
** CT = Contact time, i.e., time required to collect 250 ml of water sample.

TABLE 2

EXPERIMENT II: Retention of (nitrate + nitrite)-nitrogen, orthophosphate-phosphorus and potassium by ceramic porous cups in each of four applications for various solution concentrations. The soil water samplers were subjected to a tension of 0.6 bar.

Element	Solution Concentration (mg/l)	Percent Retention In Each Application			
		A_1	A_2	A_3	A_4
		Soil Water Sampler #1 (#2)*; CT** = 54 min. (50 min.)*			
$(NO_3 + NO_2)$-N	6.9	5.7(4.3)*	2.8(0.0)	0.0(0.0)	1.4(0.0)
Ortho-P	0.209	61.5(56.7)	1.4(3.7)	2.3(1.9)	5.7(4.9)
K	31.0	8.5(8.5)	0.6(1.3)	0.0(0.0)	0.6(0.6)
		Soil Water Sampler #3 (#4); CT = 56 min. (72 min.)			
$(NO_3 + NO_2)$-N	2.9	5.6(7.4)	1.8(1.8)	1.8(0.0)	1.8(1.8)
Ortho-P	0.095	95.9(93.4)	51.1(70.5)	2.1(10.5)	8.6(4.0)
K	14.5	20.3(25.5)	3.4(5.5)	2.7(2.8)	2.1(1.4)
		Soil Water Sampler #4; CT = 70 min.			
$(NO_3 + NO_2)$-N	0.47	6.4	2.1	0.0	0.0
Ortho-P	0.062	95.2	90.3	35.5	8.1
K	11.7	28.9	5.1	5.1	3.4
		Soil Water Sampler #3; CT - 53 min.			
$(NO_3 + NO_2)$-N	0.07	0.0	0.0	+	+
Ortho-P	0.048	93.6	89.4	+	+
K	10.9	25.7	8.1	+	+

\+ Missing data.
* Data for soil water sample indicated in parentheses.
** CT = Contact time, i.e., time required to collect 250 ml of water sample.

The effect of tension on ortho-P retention by the porous cup can be best illustrated by the results of sampling unit #4 in Experiments I and II (Tables 1 and 2). Although the initial ortho-P concentration in the two applications was of the same order of magnitude (0.053 mg/l, Table 1 and 0.062, Table 2), the proportion of the element retained by the porous cup appears to be significantly higher at 0.1 bar (Table 1) than at 0.6 bar tension (Table 2). It should be noted that the contact time, i.e., time required to sample 250 millitres of water at 0.1 bar, was 435 minutes as opposed to 70 minutes at 0.6 bar. The difference in ortho-P retention by the porous cup due to applied tension may be attributed to the difference in contact time rather than tension per se.

The retention of potassium by the porous cups as a function of initial solution concentration and tension showed similar behaviour to that observed for ortho-P (Tables 1 and 2). A relatively higher proportion of potassium was retained by the cup at low tensions and low solution concentrations. As well, relative retention decreased with application.

To elaborate on effects of initial solution concentration and tension, total retention of potassium and ortho-P by the porous cups, was computed during the experiments for all applications previous to and including the one which first showed little or no retention. These calculations were straight forward for potassium since little sorption of this element occurred after the third or fourth application in all cases. However, in the case of ortho-P where a considerable proportion of the element was still retained by the cup even during the fourth application, especially in Experiment I, the percent ortho-P retention was plotted as a function of application number. Percent ortho-P retention for the subsequent applications, beyond #4, was estimated by extrapolating the graph. Similar procedures, as indicated above, were then used to determine total ortho-P retention. The results of these calculations are shown in Figure 1. Because of the limited number of data points, the results of all porous cups were plotted together and an estimated best-fit line was drawn through them.

Figure 1 clearly shows a decrease in potassium and ortho-P retention with increase in solution concentration at both 0.1 and 0.6 bar tensions. As the solution concentration increased, however, the difference in percent retention between 0.1 and 0.6 bar extracted water samples became larger. At low solution concentrations percent retention by the cups at 0.1 and 0.6 bar tensions appear to converge.

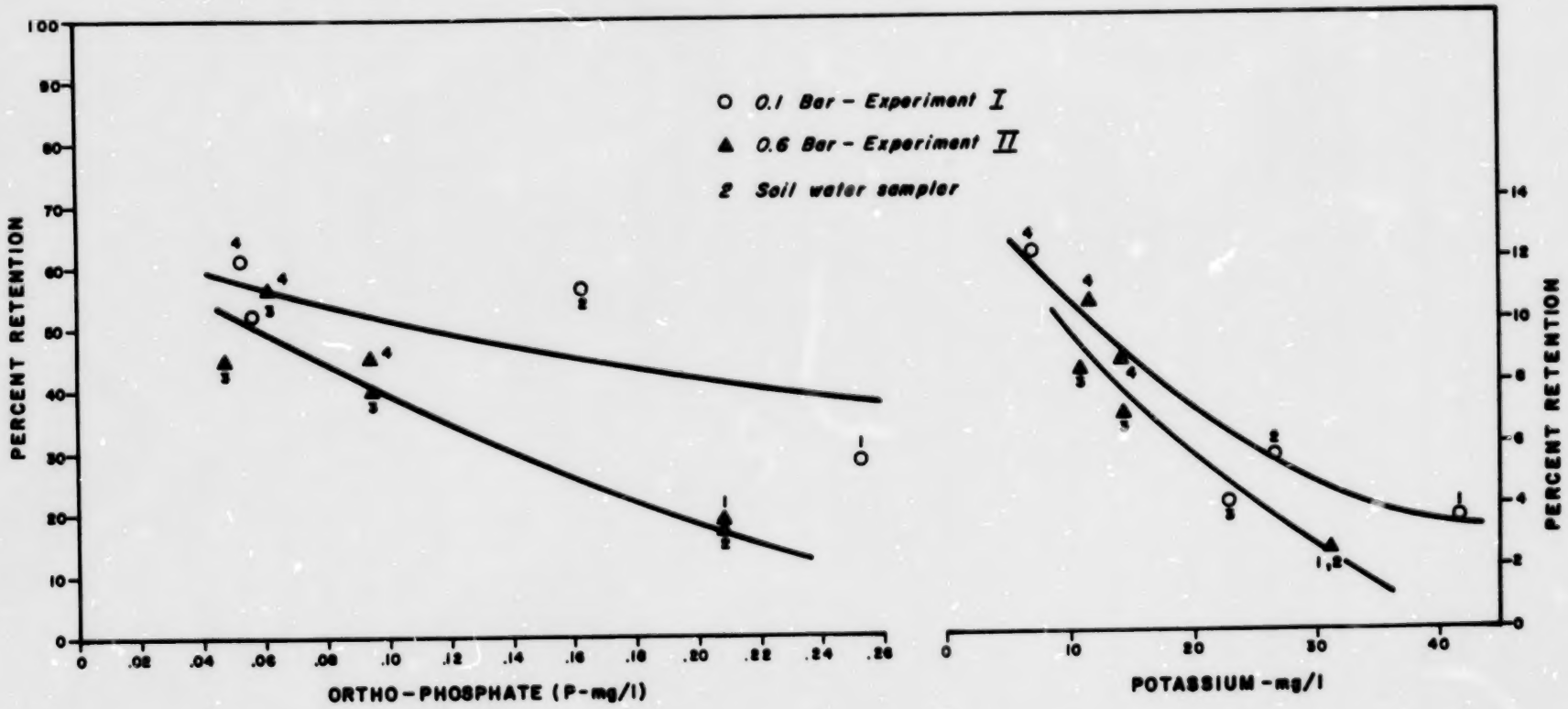

Figure 1

PERCENT RETENTION OF ORTHO-PHOSPHATE P AND POTASSIUM AS A FUNCTION OF SOLUTION CONCENTRATION FOR TWO TENSIONS

The effects of initial solution concentration and tension on $(NO_3 + NO_2)$-N retention are not very clear. However, it is apparent that $(NO_3 + NO_2)$-N concentration in the extracted water sample is subject to some change due to a porous cup (Tables 1 and 2). The decrease in $(NO_3 + NO_2)$-N concentration of extracted samples, however, cannot be the result of the elemental screening by the porous cups as suggested by Hansen and Harris (1975), since the concentration of the outside solution did not increase during the experiment. The fact that $(NO_3 + NO_2)$-N retention by the cups during the third and fourth applications (Tables 1 and 2) approaches zero or a negative value (i.e., release of element) further suggests little possibility of elemental screening. One probable cause of the decrease in $(NO_3 + NO_2)$-N concentration of the extracted water sample due to the porous cup, is the ionic transfer from a mobile solution phase flowing in the middle of a pore, to a relatively immobile phase of water near the pore walls.

3.2 Experiment III

In soil waste disposal systems such as septic tank drainfields, ionic concentration of the soil solution would fluctuate, especially in the vicinity of a seepage trench. Also, while monitoring nutrient movement in these systems on a long-term basis, porous cups would remain in contact with the soil solution. Experiment III was designed to evaluate the effects of fluctuating soil solution concentrations and "rest periods", during which the porous cup remains in contact with the soil solution at an applied tension of zero bars, on ionic concentration of water samples extracted with porous ceramic cups. The experiment was conducted at the 0.6 bar tension level only. Since phosphorus is considered to be of major concern in surface water eutrophication (Schindler, 1974), only ortho-P changes were measured. A rest period of 24 hours between several daily loading and flushing events was used. Results of Experiment III are shown in Table 3.

As expected, the highest proportions of ortho-P (11.1%) were retained during the first loading event of Day 1. This was followed by a decrease in phosphorus retention by the cup during the second loading. The twenty-four hour rest period appears to increase ortho-P retention potential. An increase in phosphate retention of 60% and 25% was observed in the first loading of the second and third day respectively, when compared with the proportion retained during the second loading of the previous day. This effect of a rest period was perhaps due to regeneration of phosphorus sorption sites as described by Sawhney and Hill (1975).

TABLE 3

Orthophosphate-phosphorus balance in EXPERIMENT III

Day	Event	Initial Solution Concentration	Quantity Of Ortho-P				Cumulative Retained/ Released
			In	Out	Retained/Released		
		mg/l	mg	mg	mg	%	mg
1	First Loading	1.15	0.287	0.255	0.032	11.1	0.032
	Second Loading	1.15	0.287	0.282	0.005	1.7	0.037
2	First Loading	1.28	0.320	0.312	0.008	2.5	0.045
	Second Loading	1.28	0.320	0.312	0.008	2.5	0.053
3	First Loading	1.36	0.340	0.330	0.010	2.9	0.063
	Second Loading	1.36	0.340	**	0.010*	2.9	0.073
4	First Flushing	.208	0.052	0.089	0.037	-71.1	0.036
	Second Flushing	.208	0.052	0.058	0.006	-11.5	0.030
5	First Flushing	.212	0.053	0.063	-0.010	-18.9	0.020
	Second Flushing	.208	0.052	0.053	-0.001	-1.9	0.019 ***
6	Loading	0.788	0.197	0.175	0.022	11.2	

* assumed value.
** data missing.
*** net retained.

The retention of ortho-P by porous cups is reversible in nature. From Table 3, it is obvious that flushing of the cup with a solution of low initial concentration released significant amounts of ortho-P retained during earlier loadings. The proportion of phosphorus released during an event, however, decreased with sequential flushing events. The release of phosphorus in response to flushing also is affected by the rest period. A break in the flushing action appears to enhance phosphorus release. For instance, following a rest period of 24 hours, 67% more ortho-P was released during the first flushing of the fifth day, than during the second flushing of the fourth day.

The results in Table 3 indicate a net retention of ortho-P by the porous cup even after four flushing events. As much as 0.019 mg of ortho-P appears to have been retained by the cup by the end of fifth day. It also appears that the cycle of retention and release of phosphorus will continue as the solution concentration fluctuates.

4. CONCLUSIONS AND RECOMMENDATIONS

A significant quantity of ortho-P and potassium may be retained by ceramic porous cups during soil water sampling. The proportion of ortho-P and K retained will, however, depend upon solution concentration as well as contact time between solution moving through pores, and porous cup material. Furthermore, the ortho-P sorption by the cup is reversible in nature. The concentration of extracted water samples may, therefore, be modified by the porous cup depending upon the previous loading and flushing history, in addition to above factors.

The $(NO_3 + NO_2)$-N retention by ceramic porous cups is believed to be mainly due to its diffusional transfer to an immobile water phase along pore walls. The mechanism of $(NO_3 + NO_2)$-N retention by a screening effect of porous cup walls does not appear to hold.

In order to minimize the effect of porous cups on extracted water samples it is recommended that (a) soil water samples be extracted at high tensions and (b) a number of water samples (two or more) be collected in succession, and samples collected later in the sequence be used to assess ionic concentration of soil solution.

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